

CLAIMS

We Claim:

1. Atorvastatin hemi-calcium Form VI and solvates thereof having a powder X-ray diffraction pattern substantially as depicted in figure 1.
2. The atorvastatin hemi-calcium Form VI and solvates thereof of claim 1 characterized by a powder X-ray diffraction pattern having peaks at 8.7, 10.0, 12.5, 17.9, 19.5, 20.9, 22.4±0.2 degrees 2θ.
3. The atorvastatin hemi-calcium Form VI and solvates thereof of claim 2 further characterized by having peaks at 7.7, 8.2, 13.8, 20.4, 21.7, 23.2, 25.5±0.2 degrees 2θ in its powder X-ray diffraction pattern.
4. The atorvastatin hemi-calcium Form VI and solvates thereof of claim 2 having a narrow particle size distribution.
5. The atorvastatin hemi-calcium Form VI and solvates thereof of claim 4 wherein all of the particles are 100 microns or less in diameter.
6. The atorvastatin hemi-calcium Form VI and solvates thereof of claim 5 wherein all of the particles are 50 microns or less in diameter.
7. A process for preparing atorvastatin hemi-calcium Form VI comprising the steps of:
 - a) solubilizing any other crystalline or amorphous form of atorvastatin hemi-calcium in acetone,
 - b) precipitating atorvastatin hemi-calcium Form VI by addition of an anti-solvent, and
 - c) separating the solid crystalline Form VI.

8. Atorvastatin hemi-calcium Form VIII and hydrates thereof having a powder X-ray diffraction pattern substantially as depicted in figure 3.
9. The atorvastatin hemi-calcium Form VIII and hydrates thereof of claim 8 characterized by a powder X-ray diffraction pattern having peaks at 9.3, 9.6, 16.3, 19.2, 20.0, 21.6, 22.4, 23.9±0.2 degrees two-theta.
10. The atorvastatin hemi-calcium Form VIII and hydrates thereof of claim 9 further characterized by having peaks at 17.1 (broad), 24.7, 25.6, 26.5±0.2 degrees two-theta in its powder X-ray diffraction pattern.
11. The atorvastatin hemi-calcium Form VIII and hydrates thereof of claim 8 having a narrow particle size distribution.
12. The atorvastatin hemi-calcium Form VIII and hydrates thereof of claim 11 wherein all of the particles are 100 microns or less in diameter.
13. The atorvastatin hemi-calcium Form VIII and hydrates thereof of claim 12 wherein all of the particles are 50 microns or less in diameter.
14. The atorvastatin hemi-calcium Form VIII and hydrates thereof of claim 8 having a water content of up to 7%.
15. The atorvastatin hemi-calcium Form VIII and hydrates thereof of claim 8 that is a trihydrate.
16. The atorvastatin hemi-calcium Form VIII and hydrates thereof of claim 8 containing up to about four moles of water.
17. The atorvastatin hemi-calcium Form VIII of claim 8 containing up to about 3% ethanol.

18. Atorvastatin hemi-calcium Form VIII and hydrates thereof with *d*-spacings of about 30.81, 18.46, 16.96, 15.39, 14.90, 12.78, 11.05, 9.58, 9.22, 7.42, 6.15, 5.43, 4.62, 4.44, and 3.98 angstroms.
19. The atorvastatin hemi-calcium Form VIII and hydrates thereof of claim 18 that produce a high resolution X-ray powder diffraction pattern substantially as shown in figure 4 when irradiated with X-rays with a wavelength of about 1.15 angstroms.
20. The atorvastatin hemi-calcium Form VIII and hydrates thereof of claim 18 having monoclinic unit cell with the following unit cell parameters: $a = 18.55\text{-}18.7 \text{ \AA}$, $b = 5.52\text{-}5.53 \text{ \AA}$, $c = 31.0\text{-}31.2 \text{ \AA}$ and $\beta = 97.5\text{-}99.5^\circ$.
21. Atorvastatin hemi-calcium Form VIII and hydrates thereof having a solid-state ^{13}C nuclear magnetic resonance spectrum substantially as depicted in figure 5.
22. The atorvastatin hemi-calcium Form VIII and hydrates thereof of claim 21 further characterized by solid-state ^{13}C nuclear magnetic resonances at 24.8, 25.2, 26.1, 119.5, 120.1, 121.8, 122.8, 126.6, 128.8, 129.2, 134.2, 135.1, 137.0, 138.3 and 139.8 parts per million.
23. The atorvastatin hemi-calcium Form VIII and hydrates thereof of claim 22 characterized by solid-state ^{13}C nuclear magnetic resonances at 17.8, 20.0, 24.8, 25.2, 26.1, 40.3, 40.8, 41.5, 43.4, 44.1, 46.1, 70.8, 73.3, 114.1, 116.0, 119.5, 120.1, 121.8, 122.8, 126.6, 128.8, 129.2, 134.2, 135.1, 137.0, 138.3, 139.8, 159.8, 166.4, 178.8 and 186.5 parts per million.
24. The atorvastatin hemi-calcium Form VIII and hydrates thereof of claim 21 having the following chemical shift differences between the lowest resonance and other resonances: 2.2, 7.0, 7.4, 8.3, 22.5, 23.0, 23.7, 25.6, 26.3, 28.3, 53.0,

55.5, 96.3, 98.2, 101.7, 102.3, 104.0, 105.0, 108.8, 111.0, 111.4, 116.4, 117.3, 119.2, 120.5, 122.0, 142.0, 148.6, 161.0 and 168.7 parts per million.

25. Atorvastatin hemi-calcium Form VIII ethanolate.
26. The atorvastatin hemi-calcium ethanolate of claim 25 containing up to about 3 % ethanol.
27. A process for preparing atorvastatin hemi-calcium Form VIII comprising the steps of:
 - a) suspending atorvastatin hemi-calcium in a mixture of ethanol and water for a period of time sufficient to convert Form V into Form VIII and
 - b) recovering Form VIII from the suspension.
28. The process of claim 27 wherein the mixture is a mixture of at least about 19 volumes of ethanol to about 1 volume of water.
29. The process of claim 27 wherein the temperature of the suspension is raised to 78-80°C before Form VIII is recovered from the suspension.
30. A process for preparing atorvastatin hemi-calcium Form VIII from atorvastatin comprising the steps of:
 - a) converting the atorvastatin into atorvastatin hemi-calcium by contacting the atorvastatin with a source of calcium ion,
 - b) suspending the atorvastatin hemi-calcium in a mixture of ethanol and water for a period of time sufficient to convert the atorvastatin hemi-calcium into Form VIII, and
 - c) recovering Form VIII from the suspension.
31. The process of claim 30 wherein the mixture is a mixture of ethanol and water in a volume ratio of about 5:1.

32. The process of claim 30 wherein additional water is added to the suspension of atorvastatin hemi-calcium before recovering Form VIII in order to increase the recovery of Form VIII from the suspension.
33. The process of claim 30 wherein the temperature of the suspension is elevated before recovering Form VIII from the suspension.
34. The process of claim 33 wherein the elevated temperature is about 78-80°C.
35. A process for preparing atorvastatin hemi-calcium containing less than 0.1% des-fluoro atorvastatin hemi-calcium comprising suspending atorvastatin hemi-calcium that contains greater than 0.1% des-fluoro atorvastatin hemi-calcium in a mixture of about 96% ethanol and about 4 % water and recovering atorvastatin hemi-calcium containing less than 0.1% des-fluoro atorvastatin hemi-calcium.
36. The process for preparing atorvastatin hemi-calcium of claim 35 wherein the atorvastatin is recovered containing less than 0.07% des-fluoro atorvastatin
37. A process for preparing atorvastatin hemi-calcium containing less than 1% *trans* atorvastatin hemi-calcium comprising suspending atorvastatin hemi-calcium that contains greater than 1 % *trans* atorvastatin hemi-calcium in a mixture of about 96% ethanol and about 4 % water and recovering atorvastatin hemi-calcium containing less than 1% *trans* atorvastatin hemi-calcium
38. The process for preparing atorvastatin hemi-calcium of claim 37 wherein the atorvastatin hemi-calcium is recovered containing less than 0.6 % *trans* atorvastatin hemi-calcium.

39. A process for preparing atorvastatin hemi-calcium Form VIII comprising the steps of:
- a) suspending atorvastatin hemi-calcium Form V in a mixture of water and a lower alcohol selected from the group consisting of 1-butanol and ethanol for a period of time to cause the conversion of Form V to Form VIII, and
 - b) recovering atorvastatin hemi-calcium Form VIII from the mixture.
40. The process of claim 39 wherein the mixture contains about 20% 1-butanol by volume.
41. The process of claim 39 wherein the lower alcohol is ethanol and the mixture contains about 4% water.
42. A process for preparing atorvastatin hemi-calcium Form VIII comprising the steps of:
- a) suspending atorvastatin hemi-calcium in ethanol for a period of time sufficient to convert it into Form VIII and
 - b) recovering Form VIII from the suspension.
43. The process of claim 42 wherein the atorvastatin hemi-calcium is Form V.
44. The process of claim 42 wherein the atorvastatin hemi-calcium is Form XII.
45. The process of claim 42 wherein the atorvastatin hemi-calcium is Form I.
46. The process of claim 42 wherein the ethanol contains about 0.5 % or less water.
47. The process of claim 46 wherein the ethanol contains about 0.2% or less water.

48. The process of claim 42 wherein the temperature of the suspension is elevated to about 78°C before Form VIII is recovered from the suspension.
49. The process of claim 48 further comprising adding methanol to the suspension before recovering Form VIII to improve the chemical purity of Form VIII recovered from the suspension.
50. Atorvastatin hemi-calcium Form IX and hydrates thereof having a powder X-ray diffraction pattern substantially as depicted in figure 6.
51. The atorvastatin hemi-calcium Form IX of claim 50 and hydrates thereof characterized by its powder X-ray diffraction pattern having peaks at 19.1, 19.9, 21.4, 22.5, 23.5±0.2 degrees 2θ.
52. The atorvastatin hemi-calcium Form IX and hydrates thereof of claim 51 further characterized by its powder X-ray diffraction pattern having peaks at 6.9, 17.0, 17.4, 18.2, 18.6±0.2 degrees two-theta.
53. The atorvastatin hemi-calcium Form IX and hydrates thereof of claim 51 containing up to 7% water.
54. An atorvastatin hemi-calcium Form IX hydrate of claim 51 containing from about one to about four moles of water.
55. The atorvastatin hemi-calcium Form IX and hydrates thereof of claim 51 having a narrow particle size distribution.
56. The atorvastatin hemi-calcium Form IX and hydrates thereof of claim 55 wherein all of the particles are 100 microns or less in diameter.

57. The atorvastatin hemi-calcium Form IX and hydrates thereof of claim 56 wherein all of the particles are 50 microns or less in diameter.
58. Atorvastatin hemi-calcium Form IX and hydrates thereof with *d*-spacings of about 30.86, 18.67, 16.91, 15.17, 12.66, 11.20, 9.50, 9.28, 8.63, 7.69, 7.38, 6.51, 5.45, 5.26, 5.20, 5.12, 4.87, 4.76, 4.63, 4.47, 4.14, 4.08, 3.78, 3.73, 3.62, and 3.58 angstroms.
59. The atorvastatin hemi-calcium Form IX and hydrates thereof of claim 58 that produce a high resolution X-ray powder diffraction pattern substantially as shown in figure 7 when irradiated with X-rays with a wavelength of about 1.15 angstroms.
60. The atorvastatin hemi-calcium Form IX and hydrates thereof of claim 58 having monoclinic unit cell with the following unit cell parameters: $a = 18.75\text{-}18.85 \text{ \AA}$, $b = 5.525\text{-}5.54 \text{ \AA}$, $c = 30.9\text{-}31.15 \text{ \AA}$ and $\beta = 96.5 \text{ to } 97.5^\circ$.
61. Atorvastatin hemi-calcium Form IX and hydrates thereof having a solid state ^{13}C nuclear magnetic resonance spectrum substantially as depicted in figure 8.
62. The atorvastatin hemi-calcium Form IX and hydrates thereof of claim 61 further characterized by solid-state ^{13}C nuclear magnetic resonances at 24.9, 26.1, 119.5, 120.2, 121.7, 122.8, 126.7, 128.6, 129.4, 134.3, 135.1, 136.8, 138.3 and 139.4 parts per million.
63. The atorvastatin hemi-calcium Form IX and hydrates thereof of claim 62 characterized by solid-state ^{13}C nuclear magnetic resonances at 18.0, 20.4, 24.9, 26.1, 40.4, 46.4, 71.0, 73.4, 114.3, 116.0, 119.5, 120.2, 121.7, 122.8, 126.7, 128.6, 129.4, 134.3, 135.1, 136.8, 138.3, 139.4, 159.9, 166.3, 178.4 and 186.6 parts per million.

64. The atorvastatin hemi-calcium Form IX and hydrates thereof of claim 61 having the following chemical shift differences between the lowest resonance and other resonances: 2.4, 6.9, 8.1, 22.4, 28.4, 53.0, 55.4, 96.3, 98.0, 101.5, 102.2, 103.7, 104.8, 108.7, 110.6, 111.4, 116.3, 117.1, 118.8, 120.3, 121.4, 141.9, 148.3, 160.4 and 168.6 parts per million.
65. Atorvastatin hemi-calcium Form IX butanolate.
66. Atorvastatin hemi-calcium Form IX containing up to about 5% butanol.
67. A process for preparing atorvastatin hemi-calcium Form IX and solvates thereof comprising the steps of:
 - a) suspending any other crystalline or amorphous form of atorvastatin hemi-calcium in 1-butanol for a period of time sufficient to convert the other form to Form IX and
 - b) recovering Form IX from the suspension.
68. The process of claim 67 wherein the other form is Form I.
69. The process of claim 67 wherein the other form is Form V.
70. The process of claim 42 wherein the other form is Form XII.
71. The process of claim 67 wherein the temperature of the suspension is elevated to the reflux temperature of 1-butanol before recovering Form IX from the suspension.
72. The process of claim 67 wherein the time sufficient to convert the other form to Form IX is about half an hour or less.

73. The process of claim 67 further comprising the step of adding an anti-solvent to the suspension before recovering Form IX in order to increase the amount of Form IX recovered from the suspension.
74. The process of claim 73 wherein the anti-solvent is selected from the group consisting of *n*-hexane, isopropanol and water.
75. A process for preparing atorvastatin hemi-calcium Form IX from Form VIII by exposing atorvastatin hemi-calcium Form VIII to an atmosphere of from about 80% to about 100% relative humidity.
76. The process of claim 75 wherein the Form VIII is exposed to the humid atmosphere for about 9 days or less.
77. The process of claim 75 wherein the Form VIII is exposed to the humid atmosphere at room temperature.
78. A process for preparing atorvastatin hemi-calcium Form IX comprising the steps of:
- a) suspending Form VIII atorvastatin hemi-calcium in ethanol for a period of time sufficient to convert the other form into Form IX and
 - b) recovering Form IX from the suspension.
79. The process of claim 78 wherein the ethanol contains about 0.5% or less water.
80. The process of claim 79 wherein the ethanol contains about 0.2% or less water.
81. The process of claim 78 wherein the temperature of the suspension is maintained at about room temperature over the time period in which the other form is converted into Form IX.

82. The process of claim 78 wherein the time period sufficient to convert the other form into Form IX is about 16 hours.
83. Atorvastatin hem-calcium Form X and solvates thereof having a powder X-ray diffraction pattern substantially as depicted in figure 9.
84. Atorvastatin hemi-calcium Form X and solvates thereof of claim 83 characterized by a powder X-ray diffraction pattern having sharp peaks at 19.1 and 19.4 ± 0.2 degrees 2θ and other peaks at 20.0 and 20.8 ± 0.2 degrees 2θ .
85. The atorvastatin hemi-calcium Form X and solvates thereof of claim 84 further characterized by having peaks at 222.8, 23.6 and 25.0 ± 0.2 degrees 2θ in its powder X-ray diffraction pattern.
86. The atorvastatin hemi-calcium Form X and solvates thereof of claim 83 containing up to about 5% water.
87. The atorvastatin hemi-calcium Form X and solvates thereof of claim 83 containing one to three moles of water.
88. Atorvastatin hemi-calcium Form X and solvates thereof containing up to about 2% ethanol.
89. The atorvastatin hemi-calcium Form X and solvates thereof of claim 83 having a narrow particle size distribution.
90. The atorvastatin hemi-calcium Form X and solvates thereof of claim 89 wherein all of the particles are 100 microns or less in diameter.
91. The atorvastatin hemi-calcium Form X and solvates thereof of claim 90 wherein all of the particles are 50 microns or less in diameter.

92. Atorvastatin hemi-calcium Form X and solvates thereof with *d*-spacings of about 30.63, 18.49, 16.66, 15.12, 12.49, 11.19, 10.20, 9.38, 9.24, 9.13, 8.58, 7.64, 7.36, 7.26, 6.81, 6.50, 6.16, 5.91, 5.24, 5.19, 5.06, 4.86, 4.74, 4.65, 4.61, 4.56, 4.12, 4.05, 3.93, 3.90, and 3.77 angstroms.
93. The atorvastatin hemi-calcium Form X and solvates thereof of claim 92 that produce a high resolution X-ray powder diffraction pattern substantially as shown in figure 10 when irradiated with X-rays with a wavelength of about 1.15 angstroms.
94. The atorvastatin hemi-calcium Form X and solvates thereof of claim 92 having a monoclinic unit cell with the following unit cell parameters: $a = 18.55\text{-}18.65 \text{ \AA}$, $b = 5.52\text{-}5.53 \text{ \AA}$, $c = 30.7\text{-}30.85 \text{ \AA}$ and $\beta = 95.7 \text{ to } 96.7^\circ$.
95. Atorvastatin hemi-calcium Form X and solvates thereof having a solid state ^{13}C nuclear magnetic resonance spectrum substantially as depicted in figure 11.
96. The atorvastatin hemi-calcium Form X and solvates thereof of claim 95 further characterized by solid-state ^{13}C nuclear magnetic resonances at 24.9, 119.5, 122.4, 126.7, 128.9, 134.5, 138.0, 159.4 and 166.2 parts per million.
97. The atorvastatin hemi-calcium Form X and solvates thereof of claim 96 characterized by solid-state ^{13}C nuclear magnetic resonances at 17.7, 18.7, 19.6, 20.6, 24.9, 43.4, 63.1, 66.2, 67.5, 71.1, 115.9, 119.5, 122.4, 126.7, 128.9, 134.5, 138.0, 159.4, 166.2, 179.3, 181.1, 184.3 and 186.1 parts per million.
98. The atorvastatin hemi-calcium Form X and solvates thereof of claim 95 having the following chemical shift differences between the lowest resonance and other resonances: 1.0, 1.9, 2.9, 7.2, 25.7, 45.4, 48.5, 49.8, 53.4, 98.2, 101.8,

104.7, 109.0, 111.2, 116.8, 120.3, 141.7, 148.5, 161.6, 163.4, 166.6 and 168.4 parts per million.

99. A process for preparing atorvastatin hemi-calcium Form X comprising the steps of:
- a) suspending any other crystalline or amorphous form of atorvastatin hemi-calcium in a mixture of ethanol and water for a period of time sufficient to convert the other form into Form X and
 - b) recovering Form X from the suspension.
100. The process of claim 99 wherein the suspension is heated to the reflux temperature of the ethanol-water mixture before recovery of Form X from the suspension.
101. The process of claim 99 wherein the time sufficient to convert the other form into Form X is about an hour.
102. The process of claim 99 wherein the mixture contains about six parts ethanol to one part water.
103. The process of claim 99 wherein the mixture contains about five parts ethanol to one part water.
104. Atorvastatin hemi-calcium Form XI and solvates thereof having a powder X-ray diffraction pattern substantially as depicted in figure 12.
105. The atorvastatin hemi-calcium Form XI and solvates thereof of claim 104 characterized by PXRD peaks at 3.2, 3.7, 5.1, 6.3, 7.8, 8.6, 9.8, 11.2, 11.8, 12.4, 15.4, 18.7, 19.9, 24.0 ± 0.2 degrees two-theta.

106. The atorvastatin hemi-calcium Form XI and solvates thereof of claim 104 having a narrow particle size distribution.
107. The atorvastatin hemi-calcium Form XI and solvates thereof of claim 106 wherein all of the particles are 100 microns or less in diameter.
108. The atorvastatin hemi-calcium Form XI and solvates thereof of claim 107 wherein all of the particles are 50 microns or less in diameter.
109. A process for preparing atorvastatin hemi-calcium Form XI comprising the steps of:
- a) suspending atorvastatin hemi-calcium in methyl ethyl ketone at room temperature for a period of time sufficient to cause the conversion into atorvastatin hemi-calcium Form XI, and
 - b) recovering atorvastatin hemi-calcium Form XI from the suspension.
110. The process for preparing atorvastatin hemi-calcium Form XI of claim 109 wherein the atorvastatin hemi-calcium is Form V.
111. A process for preparing atorvastatin hemi-calcium Form XI comprising the steps of dissolving atorvastatin hemi-calcium in isopropyl alcohol at elevated temperature to form a solution of atorvastatin hemi-calcium, cooling the solution until it gels and then drying the gel to obtain atorvastatin hemi-calcium Form XI.
112. Atorvastatin hemi-calcium Form XII and solvates thereof characterized by a powder X-ray diffraction pattern having peaks at 8.0, 8.4, 11.8, 18.2, 19.0 ± 0.2 degrees 2θ .
113. The atorvastatin hemi-calcium Form XII and solvates thereof of claim 112 having a narrow particle size distribution.

114. The atorvastatin hemi-calcium Form XII and solvates thereof of claim 113 wherein all of the particles are 100 microns or less in diameter.
115. The atorvastatin hemi-calcium Form XII and solvates thereof of claim 114 wherein all of the particles are 50 microns or less in diameter.
116. A process for preparing atorvastatin hemi-calcium Form XII comprising the steps of:
 - a) suspending [R-(R*,R*)]-2-(4-fluorophenyl)- β , δ -dioxane-5-(1-methylethyl)-3-phenyl-4-[(phenylamino)carbonyl]-1H-pyrrole-1-*tert*-butylheptanoic ester in ethanol,
 - b) deprotecting the [R-(R*,R*)]-2-(4-fluorophenyl)- β , δ -dioxane-5-(1-methylethyl)-3-phenyl-4-[(phenylamino)carbonyl]-1H-pyrrole-1-*tert*-butylheptanoic ester by adding hydrochloric acid to the suspension, thereby forming a solution of atorvastatin ester derivatives in ethanol,
 - c) adding calcium hydroxide to the solution, thereby forming a solution of atorvastatin hemi-calcium in ethanol,
 - d) optionally removing any excess calcium hydroxide, and
 - e) precipitating atorvastatin hemi-calcium from the solution as Form XII.
117. A process for preparing atorvastatin hemi-calcium Form I comprising the steps of:
 - a) suspending any other form of atorvastatin hemi-calcium in water for a period of time sufficient to convert the other form into Form I and
 - b) recovering Form I from the suspension.
118. A process for preparing atorvastatin hemi-calcium Form II comprising the steps of:

- a) suspending [R-(R*,R*)]-2-(4-fluorophenyl)- β , δ -dioxane-5-(1-methylethyl)-3-phenyl-4-[(phenylamino)carbonyl]-1H-pyrrole-1-*tert*-butylheptanoic ester in methanol,
- b) deprotecting the [R-(R*,R*)]-2-(4-fluorophenyl)- β , δ -dioxane-5-(1-methylethyl)-3-phenyl-4-[(phenylamino)carbonyl]-1H-pyrrole-1-*tert*-butylheptanoic ester by adding hydrochloric acid to the suspension, thereby forming a solution of atorvastatin ester derivatives in methanol,
- c) adding calcium hydroxide to the solution, thereby forming a solution of atorvastatin hemi-calcium in methanol,
- d) optionally removing any excess calcium hydroxide, and
- e) precipitating atorvastatin hemi-calcium from the solution as Form II.

119. A process for preparing amorphous hemi-calcium comprising the steps of:
 - a) suspending a crystalline form of atorvastatin hemi-calcium in acetonitrile,
 - b) sonicating the suspension for a period of time sufficient to convert the crystalline form to amorphous atorvastatin hemi-calcium, and
 - c) recovering amorphous atorvastatin hemi-calcium from the suspension.
120. The process of claim 119 wherein the crystalline form of atorvastatin hemi-calcium is Form VII.
121. The process of claim 119 wherein the crystalline form of atorvastatin hemi-calcium is Form I.
122. The process of claim 119 wherein the suspension is sonicated for a period of from about 1 to about 3 minutes.
123. The process of claim 119 wherein the suspension is sonicated at room temperature.

124. A process for preparing atorvastatin hemi-calcium Form IV comprising the steps of:
 - a) suspending atorvastatin hemi-calcium Form I in 1-butanol for a period of time sufficient to convert Form I into Form IV and
 - b) recovering Form IV from the suspension.
125. The process of claim 124 wherein the suspension is maintained at room temperature for the period time in which Form I is converted into Form IV.
126. The process of claim 124 wherein the time sufficient to convert Form I into Form IV is about 24 h.
127. A process for preparing atorvastatin hemi-calcium Form IV comprising the steps of:
 - a) suspending atorvastatin hemi-calcium Form V in a mixture of ethanol and water for a period of time sufficient to convert Form V into Form IV and
 - b) recovering Form IV from the suspension.
128. The process of claim 127 wherein the temperature of the suspension is elevated to about 50°C before recovering Form IV from the suspension.
129. The process of claim 127 wherein the period of time sufficient to convert Form V into Form IV is about one hour.
130. The process of claim 127 wherein the mixture contains about 15% water.
131. A process of preparing atorvastatin hemi-calcium Form IV comprising the steps of:
 - a) suspending atorvastatin hemi-calcium Form V in methanol for a period of time sufficient to convert Form V into Form IV, and
 - b) recovering Form IV from the suspension.

132. The process of claim 131 wherein the suspension is maintained at a temperature of from about room temperature to the reflux temperature of methanol for the period of time in which Form Vis converted into Form IV.
133. The process of claim 131 wherein the period of time sufficient to convert the other form into Form IV is from about 1 hour to about 20 hours.
134. A process for preparing atorvastatin hemi-calcium Form V comprising the steps of:
- suspending [R-(R*,R*)]-2-(4-fluorophenyl)- β , δ -dioxane-5-(1-methylethyl)-3-phenyl-4-[(phenylamino)carbonyl]-1H-pyrrole-1-*tert*-butylheptanoic acid ester in ethanol,
 - deprotecting the [R-(R*,R*)]-2-(4-fluorophenyl)- β , δ -dioxane-5-(1-methylethyl)-3-phenyl-4-[(phenylamino)carbonyl]-1H-pyrrole-1-*tert*-butylheptanoic ester by adding hydrochloric acid to the suspension, thereby forming a solution of atorvastatin lactone and [R-(R*,R*)]-2-(4-fluorophenyl)- β , δ -dihydroxy-5-(1-methylethyl)-3-phenyl-4-[(phenylamino)carbonyl]-1H-pyrrole-1-*tert*-butylheptanoic acid ester in ethanol,
 - adding calcium hydroxide to the solution, thereby forming a solution of atorvastatin hemi-calcium in ethanol,
 - precipitating atorvastatin hemi-calcium from the solution, and
 - drying the precipitated atorvastatin hemi-calcium to obtain atorvastatin hemi-calcium as Form V.
135. A process for purifying atorvastatin hemi-calcium Form V comprising suspending the atorvastatin hemi-calcium Form V in a mixture of ethanol and water and recovering Form V from the mixture in greater purity.

136. The process of claim 135 wherein the mixture comprises from about 10 % water and about 90% ethanol by volume.
137. A process for preparing amorphous atorvastatin hemi-calcium comprising the steps of:
- a) contacting any crystalline form of atorvastatin hemi-calcium with acetone for a period of time sufficient to convert the crystalline form into amorphous atorvastatin hemi-calcium and
 - b) separating solid amorphous atorvastatin hemi-calcium from the acetone.
138. The process for preparing amorphous atorvastatin hemi-calcium of claim 137 wherein the crystalline form of atorvastatin hemi-calcium dissolves in the acetone to yield a substantially clear solution and further wherein solid amorphous atorvastatin hemi-calcium is precipitated from the substantially clear solution.
139. A process of claim 137 wherein the crystalline form of atorvastatin hemi-calcium is Form V.
140. The process of claim 137 wherein the crystalline form of atorvastatin hemi-calcium and acetone are contacted at room temperature.
141. The process of claim 137 wherein the period of time sufficient to convert the crystalline form into amorphous atorvastatin hemi-calcium is about 16 hours.
142. A process for preparing amorphous atorvastatin hemi-calcium by ball milling any crystalline form of atorvastatin hemi-calcium.
143. The process of claim 142 wherein the crystalline form of atorvastatin hemi-calcium is selected from the group consisting of Form I, Form V and Form VIII.

144. A pharmaceutical composition comprising atorvastatin hemi-calcium Form VI, VIII, IX, X, XI, XII or a mixture thereof.
145. Use of atorvastatin Form VI, VIII, IX, X, XI, XII or mixtures thereof, to prepare a pharmaceutical dosage form.
146. A pharmaceutical dosage form comprising atorvastatin hemi-calcium Form VI, VIII, IX, X, XI, XII or mixtures thereof.